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Effect of Exhaust Gas on Natural Stone Tablets, a Laboratory Experiment

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Abstract

8 different natural stone types were exposed to exhaust gas under laboratory conditions to assess urban stone damage. 3 cm in diameter cylindrical test specimens were made from travertine, non-porous limestone, limestone, rhyolite tuff, sandstone, andesite, granite and marble. The samples were exposed for 1, 2, 4 and 8 hours to exhaust gas that was generated by compression ignition internal combustion engine. The exhaust emission was measured. The operating conditions of the engine were documented and several parameters (weight, density, ultrasonic pulse velocity, capillary water absorption, porosity) were measured before and after exhaust gas exposure. The tests indicate that despite the deposition of soot on the surface a significant material loss was recorded at rhyolite tuff (2m%) and at andesite (1m%). The penetration depth of soot was also different for different lithologies. A correlation was found between the ultrasonic pulse velocity and density of tested stones.

Keywords

diesel engine, exhaust gas, natural stone, porosity, weight loss

1 Introduction

Natural stones are frequently used in constructions and applied outside and inside. One of the key problems of external use is the discoloration and damage of building facades. The colour changes can be attributed to air pollution, in the form of deposition of pollutants which lead to blackening of building stone [1–3]. The blackening process clearly related to particulate matter [4]. The blackening and formation of soiling layer have been described for various stone types including marble [5–6], limestone [4, 7, 8], travertine [9] and even on volcanic rocks [10–11]. The soiling is related to particle deposition and incorporation into the newly formed gypsum layers [12] and also causes other changes in physical properties such as strength that influences durability [3]. The colour change reflects air quality and thus millennium long changes can be also recorded [13]. In the past decades vehicles were the main causes of urban stone decay, however air pollution can cause damage in stone structures located in rural settings [11, 14]. The colour change and sulfation process can be modelled under laboratory conditions where carbonate samples are exposed to exhaust gas (particulates) and SOx [15]. The changes can be recorded by testing newly formed mineral phases and also by measuring colour changes [2].

Our basic aim was to investigate the aesthetic effect of air pollution derived from road vehicle's engine on stones widely used for construction and decoration. The main question is how this induced pollution contribute to accelerated weathering and how the exhaust gas related particulate matters influence the colour of stone slabs. Similar chamber test was applied to evaluate the role of particulate matter coming from vehicular sources on stone sulfation [15]. This paper focuses on changes of physical properties rather than on mineralogical alterations of stone slabs having different composition.

2 Materials

The tests were carried out on 8 different stone types. These types of stones have been chosen because they are used widely and they have very different physical and chemical properties. The tested natural stones are widely used

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in buildings and structures as dimension and ornamental stones in Hungary [16–17]. Except for Carrara marble from Italy and Mauthausen granite from Austria, the tested 6 other stone types were obtained from Hungarian quarries. Cylindrical tests specimens with a diameter of 3 cm were used for the tests (Fig. 1).

Selected types of stones (and their localities of origin) are given here (from left to right on Fig. 1):

top row:

- porous limestone (Sóskút)
- rhyolite tuff (Sirok)
- sandstone (Romhány)
- travertine (Süttő)

bottom row:

- granite (Mauthausen)
- andesite (Gyöngyös)
- non-porous limestone (Tardos)
- marble (Carrara)

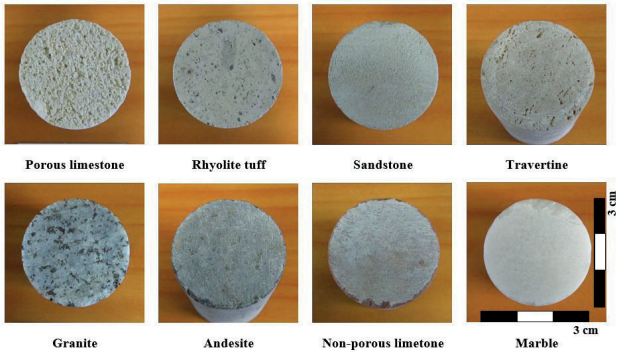

Fig. 1 Stone types (see explanation in the text)

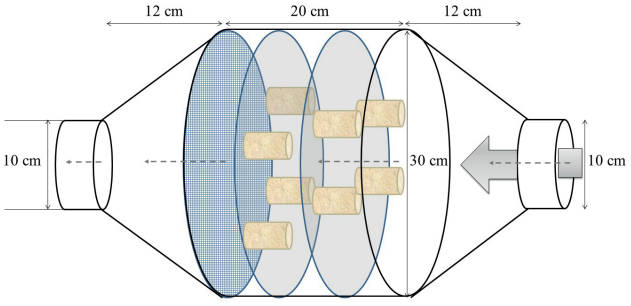

Fig. 2 Cylindrical samples in the exposure chamber

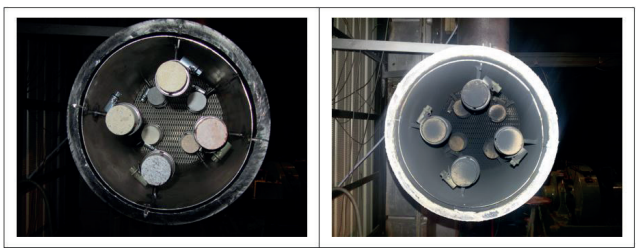

Fig. 3 Prior to and after exhaust gas exposure

Table 1 Measured emission data and temperature

	1 h	2 h	4 h	8 h
O_2 [%]	12.9	12.9	13.01	12.9
CO_2 [%]	5.919	6.023	6.101	6.107
CO [ppm]	142.7	141.3	139.8	144.7
CH [ppm]	59.9	57.8	61.4	62.3
NO_x [ppm]	680.1	688.2	693.4	716.8
NO [ppm]	537.2	540.5	542.0	553.4
k value [m^{-1}]	0.065	0.076	0.072	0.077
Temperature [°C]	245.0	244.5	247.3	246.9

3 Methods

3.1 Pollution of stones – exposure chamber

A block of 8 different stone types was placed in a chamber, which was built in the exhaust gas system of a compression ignition internal combustion engine, so the exhaust gas of the engine was led through the chamber. In this case the exhaust stream could contact directly to the surface of the material specimens. The location of the samples in the exposure chamber is given on Fig. 2, while samples prior and after the test are shown on Fig. 3.

A compression ignition engine was used to generate exhaust gas to pollute directly the stones. The most important data of the engine are listed in Table 1. This engine was running on conventional diesel, which was purchased from a petrol station in Budapest.

The engine was operated for 1, 2, 4 and 8 hours at one operating point. Operating conditions (1300 r/min and 50% load) of the RÁBA D10 UTSLL 160, EuroII engine were controlled and the temperature inside the chamber, gas phase components and k absorption coefficient were continuously measured during the test. The engine operating point was chosen due to the higher k value [18–21]. The fuel used was gas oil complying with MSZ EN 590 from MOL fuel station. The fuel consumption was 3,91 g/s and the mass flow of exhaust gas was approximately 475 kg/h.

3.2 Laboratory tests

Measurements regarding the mass of the stones before and after the pollution have been carried out with the help of the analytical balance (Kern AES Analytical Balance).

Ultrasonic pulse velocity values were measured by 5 cm in diameter Pundit transmitter and receiver ultrasonic velocity tester. The test procedure is described in details by EN 14579.

The pore distribution was evaluated by a mercury porosimeter (Carlo Erba - GFZ Potsdam) at University of Goettingen, Germany. Capillary water absorption tests

were made following the guidelines given by European Norm (EN 1925) on tests specimens of each lithotypes.

The penetration depth of soot was recorded based on the visual inspection of specimens that were broken into halves during indirect tensile strength test (Brasilian).

4 Results and discussion

4.1 Physical properties

The saturation of porous stones (porous limestone, rhyolite tuff, sandstone and travertine) was shorter it took 8.5 hours during capillary water absorption tests (Fig. 4), while the saturation of non-porous stones (granite, andesite, non-porous limestone, marble) took at least 16 hours (Fig. 5). The porous limestone absorbed the highest amount of water at the shortest period of time. The water absorption also caused colour changes. The most visible one was observed at rhyolite tuff (Fig. 4).

Water absorption was higher on porous limestone, rhyolite tuff and sandstone.

The lowest density of studied stones was measured at porous limestone, while the highest one was documented in granite (Fig. 6).

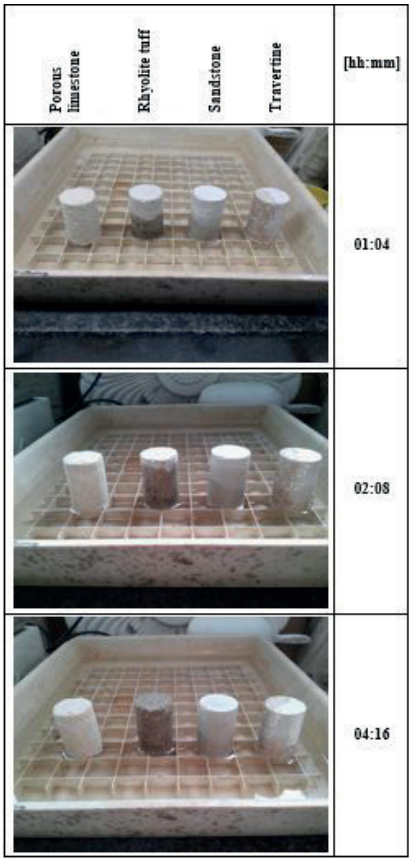

Fig. 4 Capillary water absorption of stones (porous limestone, rhyolite tuff, sandstone and travertine) as time progresses

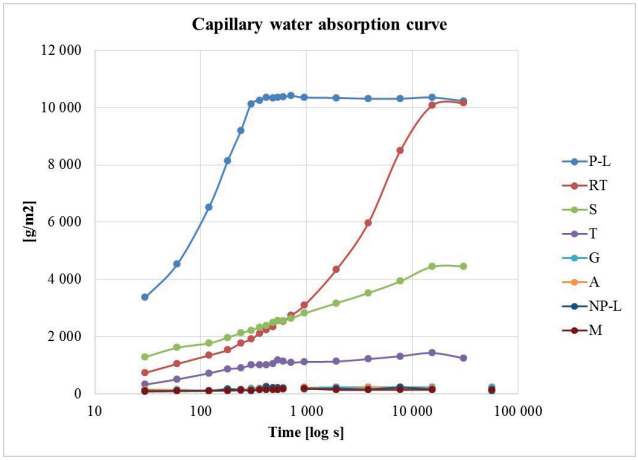

Fig. 5 Capillary water absorption curves (porous limestone - blue, rhyolite tuff - red, sandstone – green and travertine - purple)

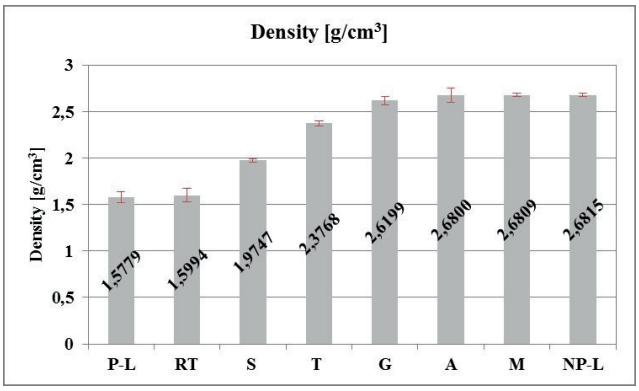

Fig. 6 Density of selected stones (P-L: porous limestone, RT: rhyolite tuff, S: sandstone, T: travertine, G: granite, A: andesite, M: marble, NP-L: non-porous limestone)

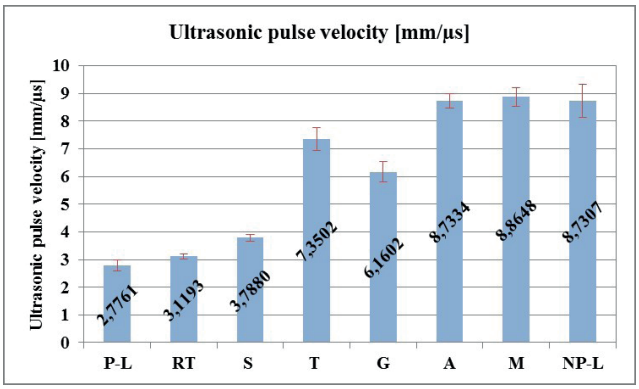

Fig. 7 Ultrasonic pulse velocity

The ultrasonic pulse velocity of marble was the highest, while has been plotted in the next figure (Fig. 7), while stones are in the same order than it was the case of Fig. 6.

Figure 8 shows density in function the ultrasonic pulse velocity. It can be see both the own measurement results and the results derived from the [22–23]. Tested highly porous, low density stones (porous limestone, rhyolite

tuff and sandstone) are found in a distinct field that overlaps with the data obtained from literature. The measured higher density stones have higher UPV values than the ones mentioned in the previous works [23].

In order to be able to investigate the values of density and ultrasonic pulse velocity a regression analysis was made for three tested stone types: porous limestone, travertine and non-porous limestone (Table 2). These equations show that there is a good correlation between obtained values and that of the previous studies [22, 23, 24].

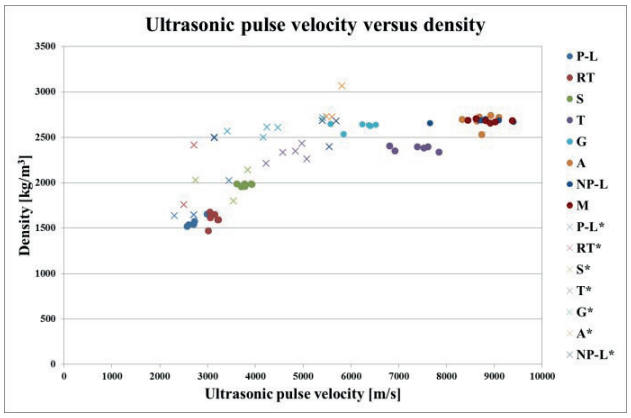

Fig. 8 Ultrasonic pulse velocity versus density (this study: •, literature data: x [22–23])

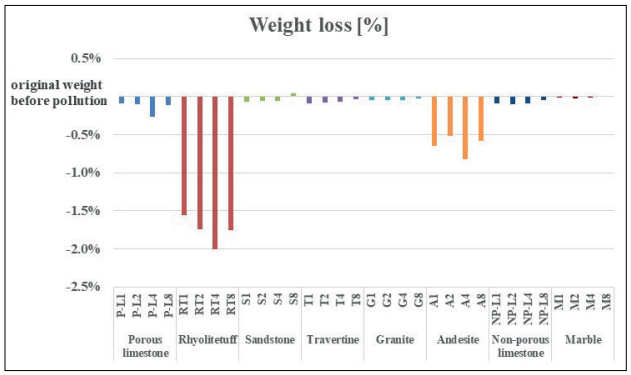

Fig. 9 Weight loss in percentage of the original stone weight before the 1, 2, 4 and 8 hours long pollution treatments

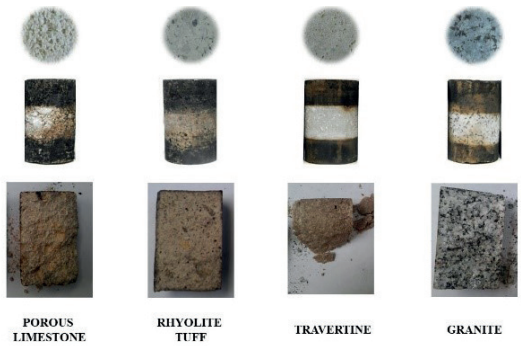

Fig. 10 Penetration depth in 4 different textures after 4 hours (from left to right: porous limestone, rhyolite tuff, travertine, granite)

Table 2 Correlation between ultrasonic pulse velocity (V) and density (d) of different limestones (*: this study, **: [23] ***: [22])

Stonetype	Regression equation	Coeffitient of determination (R^2)
Non-porous limestone (*)	d = 0.0297V+2429.0	0.8174
Non-porous limestone (**)	d = 0.0758V+2258.9	0.9871
Travertine (*)	d = 0.0601V+1936.2	0.8052
Travertine (**)	d = 0.2608V+1114.7	0.9162
Porous limestone(*)	d = 0.2767V+809.87	0.9467
Porous limestone (**)	d = 0.3713V+698.1	0.8552
Limestone - cubes (***)	$d_c = 0.28V_c+935.56$	0.8193
Limestone - prisms (***)	$d_p = 0.46V_p+538.49$	0.7214

Table 3 Porosity values of pure and polluted porous limestone for 4 h

	Without pollution	D4_T top	D4_F upper	D4_K middle	D4_A bottom
Porosity [Vol. %]	38.38	30.96	34.16	34.12	31.98

4.2 Changes of parameters before and after the exposure

In order to calculate the changes in weight of stones mass were measured prior to exposure trials and after each exposure period. Despite the fact that probes were discolored by the deposited soot on the stone surface, weight loss was measured at all the 8 stone types (Fig. 9).

It is probably linked to the high temperature of the exhaust gas that caused mineralogical changes. Interstitial water of layered silicates was removed and that could cause the mass loss of rhyolite tuff and andesite.

The penetration depth of soot was different for different lithologies. Pores of porous limestone, rhyolite tuff, travertine and granite were filled with particulate matter after 4 hours of exposure test (Fig. 10). Other stones with dense structure have been covered by particulate, but deep penetration was not observed by visual inspection.

Pore-size distribution of porous limestone has been investigated for fresh stone and for specimens that were subjected to exhaust gas (4 hours). Measurements were made at 4 different heights of the stone specimens: 1. top surface layer which is directly exposed to the flow of exhaust gas, 2. cylinder surface layer in the upper third part of the stone, 3. cylinder surface layer under the surface of fixing ring, 4. cylinder surface layer in the lower part of the specimens (Fig.11).

Greatest level of decrease in porosity was observed in the layers number 1 and 4, which are exposed surfaces of cylinder (Fig. 11, Table 3).

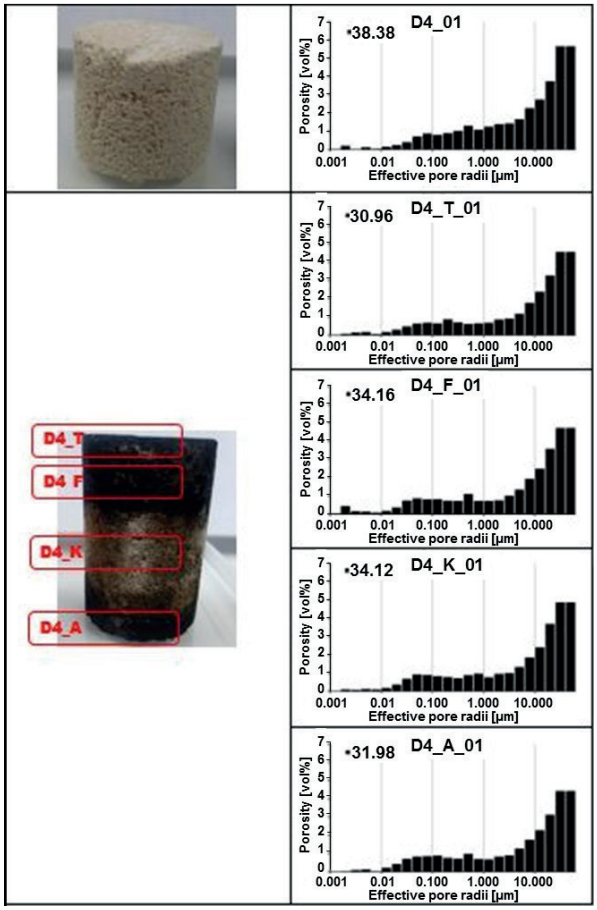

Fig. 11 Pore distribution in different layers of porous limestone before and after 4 hours long pollution

The visual inspection of colour changes suggests that the exhaust gas caused major discolouration as it was previously recorded [21], but this colour change could be different under different illuminations. It was pointed out in the previous studies of pure natural stones [25], but additional research is needed to describe the colour changes caused by exhaust gas under different illuminations.

5 Conclusions

The exposure to exhaust gas caused different weight loss of samples. The highest loss in weight was recorded at rhyolite tuff (2m%), and the mass of andesite specimens also reduced by 1m%, while the weight loss of all other lithologies were less than 0.1 m%. An increase in weight were found after 8 hours of exposure indicating the deposition of soot particles on the samples.

Our test has demonstrated the differences between 1, 2, 4 and 8 hours exposition, but this change may depend on not only time period, but also the temperature, surface roughness, porosity, in addition to the amount of soot derived from the exhaust gas.

There were clearly visible colour differences between the samples exposed for different time.

The weight loss may be related to the high temperature in the chamber and the mineralogical composition and probably mark changes in mineralogical composition and loss of interstitial water of layered silicate structures.

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